

## REPORT DOCUMENTATION PAGE

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## ABSTRACT

### CURE MONITORING OF BULK MDI-BASED POLYUREA-POLYURETHANE BY IN-SITU EMISSION FLUORESCENCE.

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# Cure Monitoring of Bulk MDI-Based Polyurea-Polyurethane by In-Situ Emission Fluorescence

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## INTRODUCTION

New generation RIM-PU formulae usually incorporate urea linkages into the pure urethane backbone so as to acquire better thermal / mechanical properties, and to achieve faster reaction rate - an essential prerequisite for automatic mass production[1]. In such systems, several competing reactions may proceed simultaneously during the cure process. Quantitative analysis of the complex mixture formed during or after curing is highly desirable to follow the reaction kinetics or to optimize the final product composition.

Many methods such as FTIR[2][3] and DSC[4] have been applied in this respect. However, most of them found difficulties to be practically useful in the real RIM system due to the sampling problem encountered in fast reaction process. In contrast, emission fluorescence can circumvent such situation and seemed most likely to be used in actual RIM-PU curing study.

In the past few years, our group launched the study of the PU cure reaction by in-situ fluorescence spectroscopy. With extrinsic sensor such as naphthyl diisocyanate (NDI), the bulk curing of MDI-based polyurethane can be mimicked[5]. Also, it was found that urea and urethane linkages from MDI were intrinsically fluorescent as formed in the DMAc solution [6]. So far, there are little study over the fluorescence of unlabeled bulk RIM-PU resin system containing both urea and urethane linkages.

In this paper, we present our recent results on the intrinsic emission fluorescence study on the model compounds and bulk curing of polyurethane-polyurea. Model compounds were dissolved in PPO of various concentration to simulate fluorophores in real RIM-PU resin which contains more than 87% of PPO. From this study, we can get information about the fluorescence peak position and concentration calibration plot for each fluorescent species. Bulk curing of a MDI-based polyurea-polyurethane resin system was carried out at room temperature and

monitored by in-situ emission fluorescence. FTIR was used to acquire the extent of reaction and to correlate with the fluorescence intensity .

## EXPERIMENTAL

Model compounds used are 1,3-diphenyl urea, carbamic acid ethyl ester (phenyl urethane) and diethyl tolyl diamine(DETDA) which contain in each molecule urea, urethane and aromatic amine chromophores respectively. All three compounds were dissolved in poly(propylene oxide)(PPO,Mn=4000) to 1% by weight, then diluted to various concentration with same PPO. For bulk curing reaction, methylene diphenyl diisocyanate was grounded to fine powder and mixed with EO-PPO(Mn=2800) and DETDA by mole ratio of 1:0.8:0.2. PPO was predried in vacuum oven at 85°C for 24hrs while DETDA was used as received. All fluorescence spectra were taken with sample sandwiched in 1/8 inch thick synthetic quartz. Bulk reaction was carried at  $20\pm1^{\circ}\text{C}$ . Curve fitting method was used to resolve the overlapped fluorescence bands The peak intensities after deconvolution was related to the extent of reaction by comparing with the FTIR results.

## RESULTS AND DISCUSSION

### 1. Model compounds Studies

From the PPO solution of model compounds, we found that urea ,urethane linkages and aromatic amine showed strong fluorescence even at relatively concentrated situation. Fluorescence peak wavelength position of urea and urethane chromophore are very close (303nm and 297nm) while those of aromatic amine appear at longer wavelength(333nm) (Figure 1).Non-linearity was observed for urea group even at quite low concentration region (Figure 2) possibly due to higher self-quenching tendencies. The fluorescence peak position of urea in PPO are about 40nm blue shifted compared in highly polar aprotic DMAc solvent [5], possibly due to higher intermolecular H-bonding for the former. Such interaction was insignificant in the case of urethane and aromatic amine. Linear relationships with concentration were observed for the PPO solution of these two model compounds.

### 2. Bulk in-situ Curing

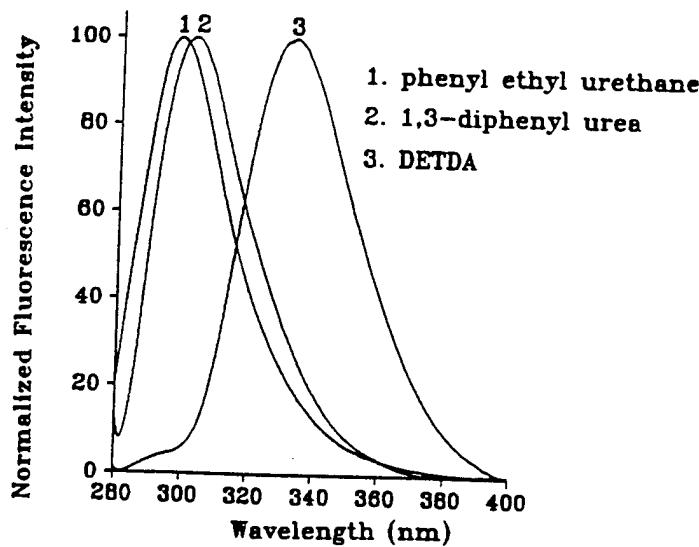
The resultant spectrum showed overlapped band (Figure 3 ) with two peaks whose positions coincided well with those predicted from model compound

study. Overlapped bands for the room temperature in-situ fluorescence can be deconvoluted and assigned to two chromophore species after curve fitting with assumption of Gaussian curve shape.(Figure 4). Peak at 327-333nm assigned to DETDA decreases drastically at the beginning of cure reaction followed by slow increase afterward. Trace of amine was left even after long reaction time up to 14hrs. This is consistent with the observation of 20% unreacted isocyanate by FTIR at the same time which is possible due to vitrification at low reaction temperature.The increase in peak intensity here might be due to viscosity effect which reduces the non-radiative relaxation. The other possibility is due to the influence of the upward trend of lower wavelength peak. Decomposition of the overlapped band is not so accurate due to unsymmetrical shape of fluorescence spectrum. Fluorescence peak at 303-310nm is a mixed band of urethane and urea groups. Decrease of peak intensity after a short period of climbing may be due to temperature rise caused by fast urea formation reaction. Another possibility is the quenching effect from urea fluorophore to either urea itself or urethane fluorophore.The extent of reaction was determined by following the disappearing rate of isocyanate group at  $2272\text{cm}^{-1}$  from FTIR data. As we correlate these fluorescence change with extent of reaction (Figure 5), the fast increase at 303nm or decrease at 333nm occurred before 20% reactioin. Since the urea amount is expected to be maximum 20% based on the molar ratio, it is reasonable to attribute the initial change to urea formation.

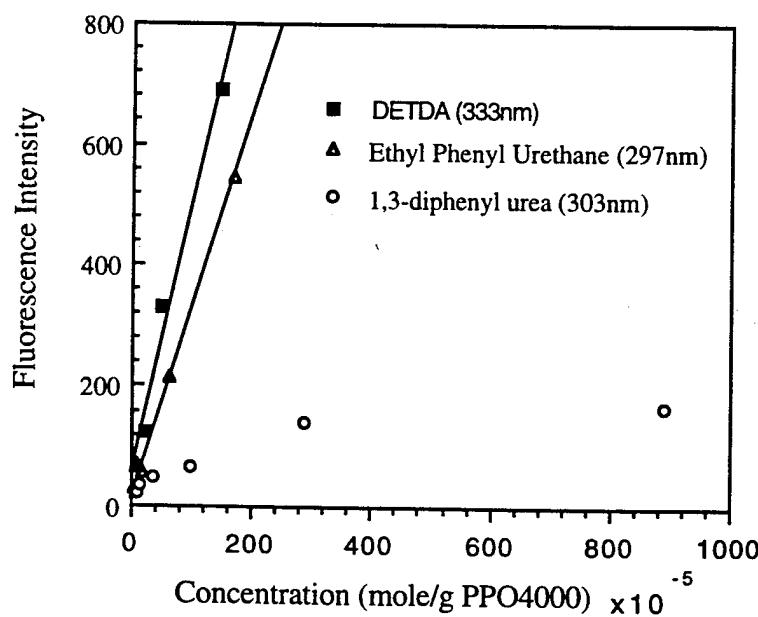
Further study on the influences of temperature, viscosity and quenching over the fluorescence in bulk resin is still proceeding in order to more quantitatively analyze the chromophore concentration change of each linkage during RIM-PU cure process.

## REFERENCES

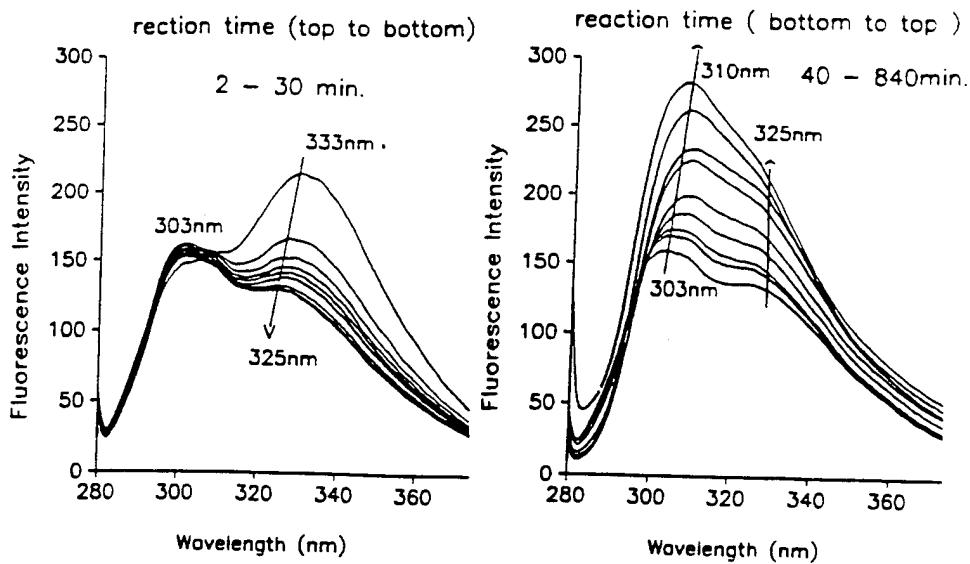
1. D.G. Schlotterbeck, et. al., *Plastic Engineering*, January, 37-40(1989).
2. A.M.Usmani, *Journal of Coatings Technology*, **56(716)**,99-103 (1984).
3. V.V.Zharkov, et. al., *Journal of Anal. Chem. USSR*, **42**, 1704 -1707(1987).
4. A.J.Ryan, J. L. Stanford and A.J.Birch, *Polymer*, **34(23)**, 4874-4881(1993)
5. X. Huang,W.Yu and C. S. P. Sung,*Macromolecules*, **23(2)**,390-398 (1990).
6. X. Sun and C. S. P. Sung, *Polymer Preprint*, ACS, Div. Polym. Chem,**35(1)**, 435 - 436 (1994).



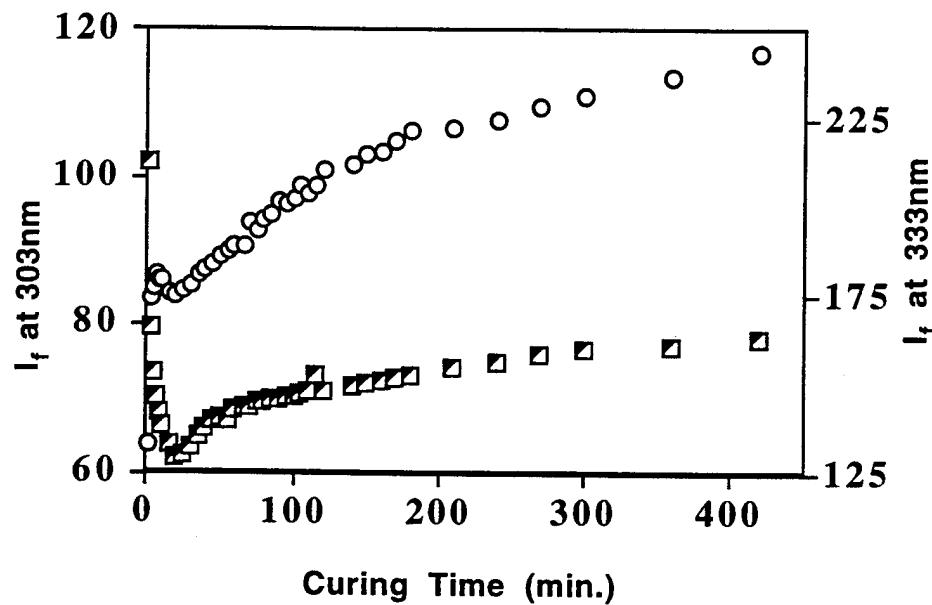
**Fig.1** Emission Fluorescence of Model Compounds in PPO  
(normalized spectrum, excited at 275nm)



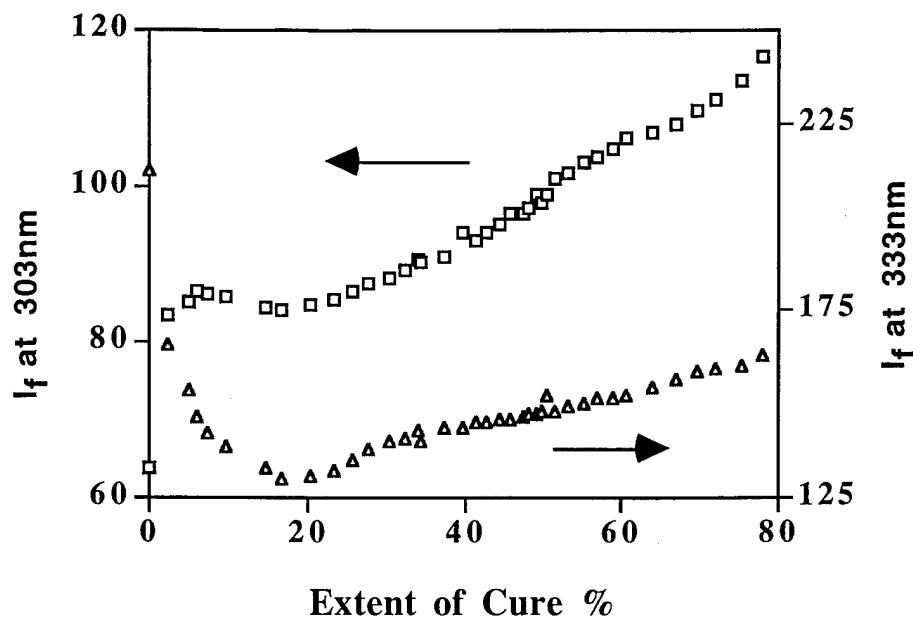
**Fig.2** Correlation plot of fluorescence intensity of PPO solution of model compounds v.s.concentration ( emission fluorescence ,excited at 275nm )



**Fig.3** In-situ emission fluorescence of RIM-PU Resin  
(MDI / EO-PPO2800 / DETDA 1:0.8:0.2 cured at 20°C, Excited at 275nm)



**Fig.4** Fluorescence intensity changes during cure ( decomposed from each overlapped spectrum in Figure 3 by curve fitting method. )



**FIG.5** Correlation of fluorescence intensity with extent of reaction.